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Exceptionally Long-Lived Luminescence from $[Cu(I)(isocyanide)_2(phen)]^+$ Complexes in Nanoporous Crystals Enables Remarkable Oxygen Gas Sensing

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Supporting Information

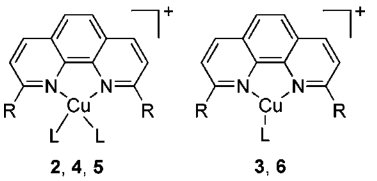
ABSTRACT: We report crystalline mixed-ligand copper complexes with phenanthroline and isocyanides with almost millesecond emission lifetimes that are efficient dioxygen sensors. The oxygen sensitivity of the prototype ($[Cu(CN\text{-}xylyl)_2(dmp)]tfpb$, dmp = 2,9-dimethyl-1,10-phenanthroline; CN-xylyl = 2,6-dimethylphenylisocyanide; tfpb = tetrakis(bis-3,5-trifluoromethylphenylborate) is 38 times better than that of $[Ru(phen)_3]tfpb_2$ (phen = 1,10-phenanthroline).

Emissive transition metal complexes dispersed in support materials have been widely utilized as molecular oxygen sensors.[1] The support materials (polymer films or sol−gels) allow diffusional dioxygen quenching of the excited state,[1c,2] but they can also produce a complicated analytical response due to the presence of nonuniform active sites. To mitigate this problem we have designed[3] self-inclusive pure crystals $[Ru(phen)_3]tfpb_2$ ((**1**), phen = 1,10-phenanthroline, tfpb = tetrakis(bis-3,5-trifluoromethylphenylborate))[3a] that contain a long-lived emissive ruthenium complex and regular void spaces to allow diffusional oxygen quenching. This prototype showed an emission quantum yield and lifetime of 0.071(2) and 0.640(4) μs (under nitrogen, respectively) and a Stern−Volmer constant (K_{SV})[4] of 2.51(2) atm^{-1}. More recently we showed that a less expensive copper complex ($[Cu(dipp)_2]tfpb$ (dipp = 2,9-diisopropyl-1,10-phenanthroline) is an oxygen sensor with an emission quantum yield of 0.019(1) (under nitrogen) and oxygen sensitivity K_{SV} = 0.308(7) atm^{-1}).[5] Substantial improvements in these parameters were realized by extending the studies to heteroleptic Cu(I) complexes containing[6] diphosphine ligands such as [Cu(xantphos)(dmp)]tfpb (dmp = 2,9-dimethyl-1,10-phenanthroline, xantphos =4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) that has an excellent quantum yield (0.66(5) under nitrogen) and a K_{SV} of 5.82(8) atm^{-1}. These metrics are comparable with the best crystalline oxygen sensors that utilize more expensive transition metals.

Because the oxygen sensitivity parameter (K_{SV}) is linearly related to the excited state lifetime,[7] its increase is critical to produce even better oxygen sensors. A change in ancillary ligand increased K_{SV} and the excited state lifetime (1.17(2) μs for $[Cu(dipp)_2]tfpb$ and 30.2(2) μs for [Cu(xantphos) (dmp)]tfpb), so we thought better π-acceptor ligands (i.e., isocyanides) might produce complexes with even longer excited state lifetimes.[8] We now report that the $[Cu(isocyanide)_n(phen\text{-}derivative)]X$ (n = 1 or 2, X = BF_4^- or $tfpb^-$) compounds[9] in this series are easy to synthesize, have exceptional excited state lifetimes, and exhibit excellent oxygen sensing metrics and stability.

The synthesis and characterization details of the $[Cu(isocyanide)_2(phen)]^+$ systems that we investigated are available.[10] A generic compound $[Cu(CN\text{-}xylyl)_2(dmp)]tfpb$ (**2**, CN-xylyl = 2,6-dimethylphenyl-isocyanide) was synthesized[11] from commercially available starting materials in good yields and high purity (Chart 1). Crystalline films of **2** (from methanol) were highly emissive with a quantum yield of 0.228(5) under nitrogen and found to reversibly sense oxygen, with a K_{SV} of 96(1) atm^{-1}, **nearly a factor of 20 better** than any response that we have observed previously.[6] Luminescence spectra for a crystalline film of **2** under several different oxygen concentrations in nitrogen are shown in Figure 1 while the resulting linear S−V plot is shown in Figure 2. The response time of **2** is also quite good. Pressure jump experiments gave 67(8) and 400(9) ms for 50% and 95% returns, respectively. This compound is quite usable as a sensor, but it degrades very slowly under continuous illumination, with a 0.14%/h decrease over 21 h in nitrogen.

Chart 1. Structures and Abbreviations for Complexes[a]



[a]**2**: $[Cu(CN\text{-}xylyl)_2(dmp)]tfpb$; R = methyl, L = 2,6-dimethylphenylisocyanide. **3**: $[Cu(CN\text{-}xylyl)(dbp)]tfpb$; R = *tert*-butyl, L = 2,6-dimethylphenylisocyanide. **4**: $[Cu(CN\text{-}xylyl)_2(dbp)]tfpb$; R = *tert*-butyl, L = 2,6-dimethylphenylisocyanide. **5**: $[Cu(TM4)(dbp)]_2(tfpb)_2$; R = *tert*-butyl, L = μ-2,5-dimethyl-2,5-diisocyanohexane. **6**: $[Cu(CN\text{-}xylyl)(dmp)]BF_4$; R = methyl, L = 2,6-dimethylphenylisocyanide.

Another complex that contains three coordinate Cu(I) ($[Cu(CN\text{-}xylyl)(dbp)]tfpb$ (**3**) (dbp = 2,9-di-*tert*-butyl-1,10-phenanthroline)) showed no evidence of decomposition but had a lower K_{SV} of 3.1(2) atm^{-1}. Even more promising were $[Cu(CN\text{-}xylyl)_2(dbp)]tfpb$ (**4**) and $[Cu(TM4)(dbp)]_2tfpb_2$ (**5**) (TM4 = 2,5-dimethyl, 2,5-diisocyanohexane[12]). Oxygen sensing studies for these latter compounds gave very high K_{SV}

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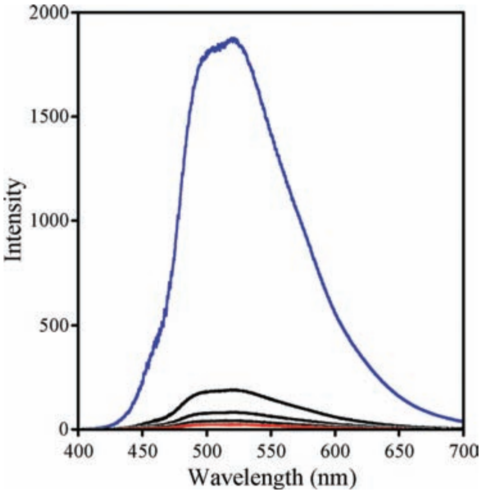

Figure 1. Uncorrected emission spectra for [Cu(CN-xylyl)$_2$(dmp)]-tfpb (**2**) excited at 375 nm under different concentrations of oxygen in nitrogen. The spectra under pure nitrogen and pure oxygen are shown in blue and red, respectively. Mole fraction of oxygen in nitrogen from top to bottom is 0, 0.095, 0.241, 0.467, 1.0.

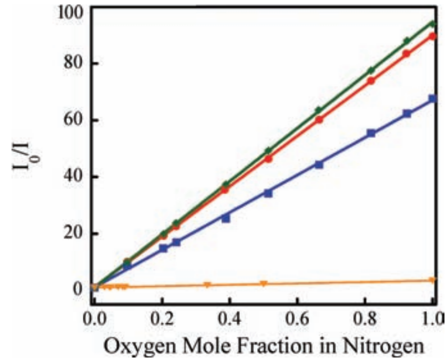

Figure 2. Intensity Stern–Volmer plots for oxygen/nitrogen gas mixtures; lines are linear regression fits. Top to bottom: green points and line, (**2**); red, (**5**); blue, (**4**); orange, (**1**). In each case three cycles were collected over a 15 h period for each sample; one cycle is displayed for clarity.

values of 65(2) and 91.9(3) atm^{-1}, respectively. Compared with **2**, the stability of compound **5** under continuous illumination is improved by nearly a factor of 3 (0.048%/h) under nitrogen or air.

The K_{SV} values for **2**, **4**, and **5** are highly reproducible with small standard deviations that encompass three determinations each of two different samples prepared and measured over a period of up to 15 days. Crystalline films that were stored in air for up to a year gave sensing metrics virtually identical to those of samples prepared and used immediately. The nearly identical K_{SV} values measured for single crystals and the corresponding crystalline film suggest that in each case they have identical crystal structures.

The reasons the [Cu(isocyanide)$_2$(phen)]$^+$ systems exhibit enhanced oxygen sensing were investigated by a combination of X-ray crystallography, lifetime measurements, variable temperature emission spectroscopy, and electrochemistry. Previous X-ray crystallography results for similar compounds[10] showed that void space is necessary for oxygen sensing[5,6] as exemplified here by the lack of void space and sensing ability observed for [Cu(CN-xylyl)(dmp)]BF$_4$ (**6**). The new isocyanide containing compounds that sense dioxygen have small to moderate void space values (2–4%) that are similar to those previously characterized[5,6] so the large increase in K_{SV} is likely due to the dramatic increase in room temperature excited state lifetimes (309, 106, and 1204 μs under nitrogen, for **2**, **4**, and **5**, respectively) that we observed. These room temperature lifetimes are unprecedented for solid state ionic Cu(I)–phen complexes[13] and are especially surprising as the isocyanide complexes exhibit minimal steric hindrance at the metal; even the three coordinate Cu(I) complex (**3**) has a long lifetime (335 μs).[14]

The model first proposed for the solution photophysics of phen-derivative copper(I) complexes suggested that increases in the lifetime and quantum yield[14,15] result when substantial steric hindrance at the metal or solid state interactions enforce the pseudotetrahedral ground state geometry and minimize distortion of the emissive metal-to-ligand charge transfer (MLCT) excited state to a pseudosquare planar geometry. Even allowing for some restricted distortion in the solid, the long lifetimes observed for the minimally hindered isocyanide complexes are, we believe, beyond the scope of this model.

The more recent[16,17] and detailed photophysics model of McMillin et al. suggests that the long-lived room temperature (rt) emission in Cu(I) phen complexes is delayed fluorescence that results from thermally activated repopulation of the emissive ^{1}MLCT singlet from the longer lived (but poorly emissive) ^{3}MLCT triplet at lower energy. For [Cu(dmp)$_2$](tfpb) the rt solid state lifetime of 0.8 μs severely limits the dioxygen quenchable delayed fluorescence. In contrast variable temperature emission spectra of the isocyanide complexes show that they have an additional, even longer lived state that can repopulate ^{1}MLCT. Evidence (below) suggests that this state is a phen centered $^3\pi-\pi^*$ triplet excited state with an intrinsically long lifetime that is efficiently quenched by dioxygen.

Emission spectra for **2** at rt, 250 K, liquid nitrogen temperature (77 K), liquid helium (4 K), and the difference spectrum between liquid nitrogen and liquid helium are shown in Figure 3. As the temperature is lowered the nearly featureless room temperature spectrum (attributed to prompt and delayed emission from ^{1}MLCT) gradually red shifts[16,18] as ^{1}MLCT emission decreases while new emissions (from ^{3}MLCT and $^3\pi-\pi^*$) grow, to be finally replaced at 4 K by the dramatic

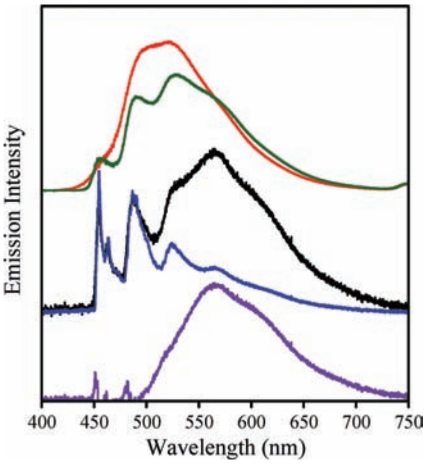

Figure 3. Emission spectra (from top to bottom) for a [Cu(CN-xylyl)$_2$(dmp)]tfpb (**2**) film at rt (red), 250 K (green), liquid nitrogen (black), liquid helium (blue), and the difference spectrum (purple) between liquid nitrogen and helium (purple).

vibrational structure (which varies with the phen substitution pattern in a given isocyanide complex) expected from only the $^3\pi-\pi^*$ phen ligand state.[19,20] At 4 K this $^3\pi-\pi^*$ state cannot repopulate either ^{1}MLCT or ^{3}MLCT that give emission at higher temperatures. In contrast emission spectra for [Cu(dipp)$_2$]tfpb and [Cu(xantphos)(dmp)]tfpb[10] show the bathochromic shift between rt and 77 K from the ^{1}MLCT to ^{3}MLCT emission change over but further cooling to 4 K leads to little additional change and especially **no development of vibronic structure.** The difference spectrum at the bottom of Figure 3 clearly shows the significant contribution from the red-shifted ^{3}MLCT emitting state in the 77 K spectrum of **2** that is absent at 4 K.

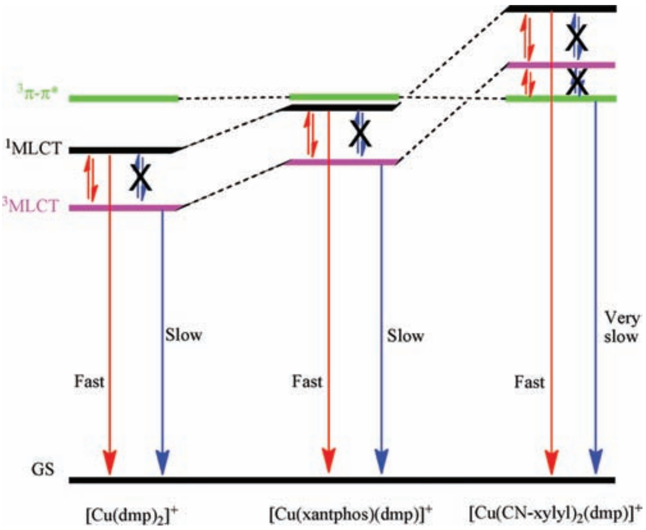

Figure 4. Diagram showing the changes in the relative energies of the lowest excited states. Nonradiative transitions are not shown; red (left) and blue arrows (right) are the dominant radiative transitions at rt and low *T*, respectively.

These changes in emission behavior for the isocyanide complexes are consistent with the McMillin photophysics model[16,17] (Figure 4) if $^3\pi-\pi^*$ is added below ^{1}MLCT* and ^{3}MLCT*. We suggest that at room temperature ^{3}MLCT* and $^3\pi-\pi^*$ are populated at the photostationary state and in rapid equilibrium with the higher energy ^{1}MLCT* state which gives delayed fluorescence with the characteristic long lifetime of the thermally equilibrated ^{3}MLCT* and $^3\pi-\pi^*$ pair. As the temperature is lowered, repopulation of first ^{1}MLCT* and then ^{3}MLCT* is deactivated so that at 4 K emission can only occur from long-lived $^3\pi-\pi^*$ with a characteristic high degree of vibronic fine structure.

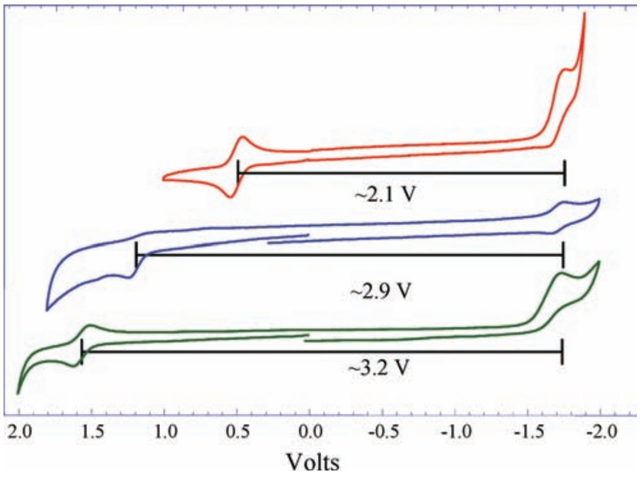

Figure 5. Cyclic voltammograms (degassed 0.1 M TBAPF$_6$ /CH$_2$Cl$_2$); from top to bottom) of [Cu(dmp)$_2$]tfpb (red), [Cu(xantphos)(dmp)]tfpb (blue), and [Cu(CN-xylyl)$_2$(dmp)]tfpb (**2**, green); horizontal bars show the approximate electrochemical band gaps.

We believe that the temperature dependent emission and the dramatic rt lifetime increase which occur upon replacement of one of the dmp ligands in [Cu(dmp)$_2$]$^+$ with first a diphosphine and then isocyanide ligands are consistent with a systematic increase in the energy of ^{1,3}MLCT* relative to the constant energies of the phen based $^3\pi-\pi^*$ state. As previous studies have shown that the energy of MLCT states shifts with changes in the redox potential of the metal we investigated the relative Cu(I)/Cu(II) stability in this series with electrochemical measurements (Figure 5). The large increase we observe in the E^0 along the series [Cu(dmp)$_2$]$^+$, [Cu(xantphos)(dmp)]$^+$, [Cu(CN-xylyl)$_2$(dmp)]$^+$ for the Cu(II)/Cu(I) couple (0.50, 1.27, 1.56 V vs AgCl/Ag) shows the significant destabilization of the Cu(II) state in the isocyanide complexes; additionally the reduction (~ −1.78 V) of the dmp ligand in these complexes does not shift. We suggest that the strongly π-accepting isocyanide ligands destabilize Cu(II) and shift the MLCT excited states above the long-lived $^3\pi-\pi^*$ energy trap. This model also readily explains the relaxed steric hindrance requirement at the Cu as the degree of distortion in the MLCT excited states is much less important in determining the lifetime once $^3\pi-\pi^*$ is the lowest. Further work to exploit the unique photophysics exhibited by these new Cu(I) isocyanide complexes for dioxygen sensing is in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis, characterization, details of X-ray structural determination, packing diagrams, cyclic voltammetry, oxygen sensing apparatus/procedures, emission spectra, lifetime plots, Stern−Volmer plots, pressure jump graph, emission spectra under liquid nitrogen and helium, solution absorption spectra, and air/nitrogen response movie. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(4) All of the K_{sv} values reported herein have been altitude corrected for the ambient atmospheric pressure (0.97 atm) in Minneapolis, MN. Additional (very small) corrections for weather related atmospheric pressure changes were not applied. Typically, we have found that these crystalline compounds have nearly identical K_{sv} values for the detection of dioxygen in aqueous solution so that the K_{sv} values reported in atm^{-1} may be provisionally converted to those appropriate in an aqueous surrounding media M^{-1} (where the oxygen concentration is expressed as molarity) by dividing by the oxygen concentration in water saturated with 1 atm of pure oxygen (1.239×10^{-3} M·atm^{-1}) at 25 °C. As an example of these calculations we give the values of K_{sv} in the various units: for **1** the previously reported (ref 3a) K_{sv} of 2.43 (mole fraction) is 2.51 atm^{-1} and 2020 M^{-1}, and for **2** (reported herein) the K_{sv} of 93 (mole fraction) is 96 atm^{-1} and 77 000 M^{-1}.

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